Final Project Report

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“Thermochemistry of Organic Radicals: Guided Ion Beam Studies”, Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Chemical Physics Program, Combustion Research, \$300,000, July 1, 2000, to June 30, 2004.

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1. Project Scope

Gas phase negative ion chemistry methods are employed to determine enthalpies of formation of hydrocarbon radicals that are important in combustion processes and to investigate the dynamics of ion–molecule reactions. Using guided ion beam tandem mass spectrometry, we measure collisional threshold energies of endoergic proton transfer and hydrogen atom transfer reactions of hydrocarbon molecules with negative reagent ions. The measured reaction threshold energies for proton transfer yield the relative gas phase acidities. In an alternative methodology, competitive collision-induced dissociation of proton-bound ion–molecule complexes provides accurate gas phase acidities relative to a reference acid. Combined with the electron affinity of the $R\cdot$ radical, the gas phase acidity yields the RH bond dissociation energy of the corresponding neutral molecule, or equivalently the enthalpy of formation of the $R\cdot$ organic radical, using equation (1).

$$D(R-H) = \Delta_{\text{acid}} H(RH) + EA(R) - IE(H) \quad (1)$$

The threshold energy for hydrogen abstraction from a hydrocarbon molecule yields its hydrogen atom affinity relative to the reagent anion, providing the RH bond dissociation energy directly. Electronic structure calculations are used to evaluate the possibility of potential energy barriers or dynamical constrictions along the reaction path, and as input for RRKM and phase space theory calculations. In newer experiments, we have measured the product velocity distributions to obtain additional information on the energetics and dynamics of the reactions.

2. Publications

The following is a list of articles that have been published or submitted since the end our previous DOE grant period and that included an acknowledgment to DOE:

“Collisional activation of the endoergic hydrogen atom transfer reaction $S^-(^2P) + H_2 \rightarrow SH^- + H$ ”, K. Rempala and K. M. Ervin, *J. Chem. Phys.* **112**, 4579-4590 (2000).

“Experimental techniques in gas phase ion thermochemistry” [Invited review article for special issue on mass spectrometry], K. M. Ervin, *Chem. Rev.* **101**, 391-444 (2001).

“Dynamics of the gas-phase reactions of fluoride ions with chloromethane”, L. A. Angel and K. M. Ervin, *J. Phys. Chem. A*, **105**, 4042-4051 (2001).

“Naphthyl radical: Negative ion photoelectron spectroscopy, Franck-Condon

simulation, and thermochemistry”, K. M. Ervin, T. M. Ramond, G. E. Davico, R. L. Schwartz, S. M. Casey, W. C. Lineberger, *J. Phys. Chem. A*, **105**, 10822-10831 (2001).

“Dynamics of the gas-phase reactions of chloride ions with fluoromethane: High excess translational activation energy for an endothermic S_N2 reaction”, Laurence A. Angel, Sandra P. Garcia, and Kent M. Ervin, *J. Am. Chem. Soc.* **124**, 336-345 (2002).

“Microcanonical analysis of the kinetic method. The meaning of the ‘apparent entropy’”, K. M. Ervin, *J. Am. Soc. Mass Spectrom.* **13**, 435-452 (2002).

“Anchoring the gas-phase acidity scale: Experiment and theory”, K. M. Ervin and V. F. DeTuri, *J. Phys. Chem. A* **106**, 9947-9956 (2002).

“Gas-phase S_N2 and bromine abstraction reactions of chloride ion with bromomethane: Reaction cross sections and energy disposal into products”, L. A. Angel and K. M. Ervin, *J. Am. Chem. Soc.* **125**, 1014-1027 (2003).

“Thermochemistry: definitions and tabulations” Ervin, K. M.; Armentrout, P. B. In *The Encyclopedia of Mass Spectrometry. Volume 1: Theory and Ion Chemistry*, Armentrout, P. B., Ed.; (Elsevier: Amsterdam, 2003) pp. 309-315.

“The only stable state of O_2^- is the $X^2\Pi_g$ ground state and it (still!) has an electron detachment energy of 0.45 eV”, K. M. Ervin, I. Anusiewicz, P. Skurski, J. Simons, and W. C. Lineberger, *J. Phys. Chem. A*, **107**, 8521-8529 (2003).

“Gas-phase hydrogen abstraction reactions of S^- with H_2 , CH_4 , and C_2H_6 ”, L. A. Angel, M. K. Dogbevia, K. M. Rempala, and K. M. Ervin, *J. Chem. Phys.* **119**, 8996-9007 (2003).

“Gas-phase reactions of iodide ion with chloromethane and bromomethane: competition between nucleophilic displacement and halogen abstraction”, L. A. Angel and K. M. Ervin, *J. Phys. Chem. A* (web release date 7/16/2004).

The following computer programs were created or substantially revised as part of this work:

“PESCAL”, Fortran program for fitting Franck-Condon profiles of electronic and photoelectron spectra, K. M. Ervin (2003). [<http://www.chem.unr.edu/~ervin/pes/>].

“ODRFIT”, Fortran program for orthogonal distance regression fitting of extended kinetic method data, K. M. Ervin and P. B. Armentrout (2004). [<http://www.chem.unr.edu/~ervin/odr/>].

“CRUNCH”, Fortran program for analysis of ion-molecule reaction cross sections, K. M. Ervin and P. B. Armentrout, version 5.005 (2004).

3. Description of Scientific Results

3.1 Biomolecular Endoergic Proton Transfer

Our first approach for measuring gas-phase acidities was to measure the threshold energy for an endoergic bimolecular proton transfer reaction, equation (2),

where HX is a reference acid of known gas phase acidity and RH is the hydrocarbon molecule of interest. The measured threshold energy for this reaction is an upper limit for the reaction endothermicity, $\Delta E_0 \leq \Delta_r H_0 = \Delta_{\text{acid}} H_0(RH) - \Delta_{\text{acid}} H_0(XH)$. When XH is a reference acid with an established gas-phase acidity, this yields an upper limit for the gas phase acidity of RH, and when the electron affinity of the radical is known, the negative ion thermochemical cycle, equation (1), in turn gives an upper limit for the R–H bond dissociation enthalpy. Anionic proton transfer reactions as in equation (2) most often have a potential energy surface with a deep well corresponding to the hydrogen-bonded proton-bound intermediate and no barriers in

either the entrance or the exit channels. Therefore, one would expect reaction (2) to proceed at the thermochemical threshold, i.e., $\Delta E_0 = \Delta_r H_0$. Indeed, a large number of endoergic ion–molecule reactions have been shown to give experimental threshold energies equal to established thermochemical endothermicities.¹ However, in applying these methods to proton transfer of small alkanols (methyl, ethyl, iso-propyl, and tert-butyl alcohol) with F^- , we found a systematic excess threshold energy of 5-9 kJ/mol that could not be explained by experimental artifacts.² More recent work on a larger set of 17 proton transfer reactions between pairs of reference acids shows similar behavior.³ In this work in preparation,³ we have shown experimentally that vibrational energy is definitely fully available to promote the reactions in addition to translational energy. We speculate that the rotational energy might not be not fully available. That would explain the magnitudes of the excess threshold energies, but there is no simple model that satisfactorily explains why rotational energy would not be active.

While most proton transfer reactions have onsets near the thermodynamic threshold, with the small excess threshold energies discussed above, a few systems show very large apparent barriers—even though the calculated potential energy surfaces show no actual energy barriers in excess of the thermochemical endoergicity. These anomalous systems appear to be associated with cases where one or both of the acids (XH or RH in reaction 2) is unable to form strong hydrogen bonds, in extreme cases forming a double-well potential. Analogies to our work on gas-phase S_N2 reactions,⁴⁻⁶ which are classic double-well systems,⁷ strongly informs our understanding of these systems. Essentially, even when the central energy barrier is well below reactants or products, it forms a “late” barrier in the sense of Polanyi rules,⁸ i.e., the R–H bond is already substantially stretched at the transition state or reaction bottleneck. That means that the reaction will be promoted more efficiently by vibrational energy than by translational energy, especially in cases where RH is a poor hydrogen bonding species and the frequency of the R–H vibration is high, leading to poor translational-to-vibrational energy transfer in the initial collision.

3.2. Competitive Threshold Collision-Induced Dissociation

Because of these issues with excess threshold energies with bimolecular proton transfer reactions, equation (2), we have pursued a different strategy that has turned out to be quite successful. The competitive threshold collision-induced dissociation (TCID) method starts with the proton-bound heterodimer intermediate of the bimolecular reaction, $X \cdot H \cdot R^-$, which is produced in the flow tube reactor source and mass selected in the first stage of the guided ion beam tandem mass spectrometer. Then we measure the cross sections for the two possible dissociation channels in equation (3),

as a function of energy, and fit the branching fraction with RRKM theory as described in section 2. The fit of the RRKM product branching fractions to the experimental cross sections provides a stringent internal test of the model.

In our first set of competitive TCID measurements published in 1999⁹ we determined the gas phase acidities of methanol, ethanol, isopropyl alcohol, and tert-butyl alcohols relative to HF and H_2O . Multiple overlapping relative acidities measurements between pairs of these species were used to construct a gas-phase acidity “ladder”, i.e., a local thermochemical network. A least-squares analysis was used to find the best values of the alcohols relative to accepted values of HF and H_2O . Merely as a test, we also anchored the network to HF alone and left the acidity of water as a free parameter. We determined $\Delta_{acid} H_0(H_2O) = 1628 \pm 2$ kJ/mol, in error by only –2

kJ/mol from the accepted value. As we stated at the time, “This indicates the internal consistency of our relative gas-phase acidity measurements is within 2 kJ/mol over a range of 80 kJ/mol [HF to H₂O], i.e., within 2.5%.”⁹ We were mostly satisfied with that level of accuracy, but in 2001 Ruscic and coworkers¹⁰ reported a revised enthalpy of formation for OH, outside the error limits compared with the previously accepted value, and this lowers the gas-phase acidity of water by 1.8 kJ/mol. The new acidity is $\Delta_{\text{acid}}H_0(\text{H}_2\text{O}) = 1627.7 \pm 0.3$ kJ/mol,^{10,11} now in near-perfect agreement with our (lower precision) result already in the literature.¹² We subsequently used the revised acidity of water to refine our alcohol acidity scale, leading to more precise values for the O–H bond dissociation enthalpies of the four alcohols, with uncertainties of ± 2 to ± 3 kJ/mol.¹² Our O–H bond dissociation energies for methanol and ethanol strongly influenced a recent IUPAC evaluation of enthalpies of formation of the “critical radicals” methoxy and ethoxy.¹³

We have since applied the competitive TCID method to determine the gas-phase acidities and R–H bond dissociation energies of diacetylene,¹⁴ longer chain-polyynes (HC_{2n}H, $n = 2, 3, 4$),¹⁵ and phenol.¹⁶ The reference acids used include hydrogen sulfide, acetaldehyde, and nitromethane. A feature of interest is that the cross sections of the two proton transfer channels cross about 1.5 eV above the thresholds. While the lower-energy channel dominates near threshold as expected, at higher activation energies the other channel overtakes it. This demonstrates that the lower-energy dissociation channel has a tighter transition state than the higher-energy channel. Indeed, the product branching as a function of energy can only be fit by using tight and loose transition state models for the two channels, respectively. This behavior strongly constrains the fits and provides a good internal test of the model. We have performed ab initio examinations of the potential energy surfaces and found double-well potentials for these systems, which corroborates the experimental findings. From this series of measurements,¹⁵ we can determine the gas-phase acidities of the polyynes. These can be combined with literature electron affinities¹⁷ of the radicals to yield preliminary bond dissociation enthalpies, as follows:

$$D_0(\text{HC}_4\text{--H}) = 543 \pm 8 \text{ kJ/mol}$$

$$D_0(\text{HC}_6\text{--H}) = 524 \pm 14 \text{ kJ/mol}$$

$$D_0(\text{HC}_8\text{--H}) = 523 \pm 8 \text{ kJ/mol}$$

The experimental uncertainties are larger than our goal of ± 4 kJ/mol primarily because only a limited number of reliable reference acids are available in the correct acidity ranges. However, these are the first experimental measurements for the whole series of polyyne C–H dissociation energies. Compared with the literature value for acetylene, $D_0(\text{HC}_2\text{--H}) = 551.2 \pm 0.1$ kJ/mol,¹⁸ the dissociation energies show that the longer-chain polyynes with six or more carbon atoms have significantly lower bond dissociation energies. That is in contrast with group additivity rules, which assume that all the CH bonds are identical to acetylene.¹⁹ These results are of potential importance for modeling acetylene pyrolysis kinetics¹⁹ and other combustion systems with polyynyl radicals as intermediates. We can explain the lower bond energies in terms of the change in the ground electronic state of the radicals, which switches from Σ to Π between HC₄ and HC₆.^{15,17,19} Because of these two low-lying electronic states, ab initio calculations of the radical energies and geometries are especially challenging and are highly dependent on the level of the calculation used, so this is definitely a case where experimental values are important. A publication on this work is in preparation, pending new analysis using Miller’s Unified Statistical Model (UST)²⁰ to treat more properly the dissociations on the double-well potential. The coding to add the UST model to our data analysis program²¹ has been recently completed and debugged.

3.3. Hydrogen Atom Abstraction

A more direct route to obtaining thermochemical information about neutral radicals is to form the radical by a hydrogen atom transfer reaction. Our first candidate for an anionic hydrogen abstraction agent has been the atomic sulfur anion, S^- , using reaction (4).

Because the $H-S^-$ bond energy is smaller than many $R-H$ bonds of interest, reaction (4) is endothermic and the reaction threshold energy may be measured by our guided ion beam techniques. We investigated reaction of S^- with H_2 previously and this showed good promise for S^- as a hydrogen abstraction agent.²² The $S^- + H_2$ reaction is well-behaved and the experimental threshold energy, obtained using fits with either an empirical threshold law or classical phase space theory, matches precisely the established endothermicity.²² Unfortunately, when we proceeded to use sulfur anion reactions to abstract hydrogen from small hydrocarbon molecules with known CH bond dissociation energies (methane, ethane, ethene, benzene),²³ the threshold energies were found to exceed the thermochemical endothermicities, indicating an effective barrier to reaction and making direct thermochemical measurements impossible. Although the isoelectronic hydrogen atom abstraction reaction by atomic chlorine is known to have a small energy barrier,²⁴ we had predicted that the strong long-range ion-induced-dipole potential would make the anionic reaction barrierless. As we subsequently verified by *ab initio* calculations of the potential energy surface, however, a small exit-channel barrier in excess of the endoergicity persists for reaction (4) when RH is a small saturated or unsaturated hydrocarbon.²³ Furthermore, the dynamics are such that a potential energy barrier in the exit channel makes activation by translational energy rather inefficient. Therefore, the measured effective threshold energies are therefore larger than the calculated potential energy barrier heights, by amounts that cannot be easily modeled.

3.4. Product Velocity Distributions

As indicated by the discussions above, in cases with an exit-channel barrier such as hydrogen atom transfer by S^- ,²³ or reactions with double-well potentials (either proton transfer^{14,15} or S_N2 ^{4,5}), the measured threshold energy for a bimolecular reaction can be larger than the endoergicity or potential energy barrier because of dynamic constraints. That is, there is effectively a reverse activation energy for translational excitation. One possible method to account for excess activation energies is to measure the disposal of energy into products via velocity distribution measurements. We modified our guided ion beam apparatus to make such measurements by time-of-flight and demonstrated such experiments first for the $Cl^- + CH_3Br \rightarrow ClCH_3 + Br^-$ S_N2 reaction.²⁵ Although not of thermochemical or combustion chemistry interest, this exothermic reaction has a classic double-well potential and the kinetic energy release had previously been studied by metastable ion dissociation,^{26,27} providing an interesting test system for comparison with literature results.²⁶⁻³⁴ At the lowest energies (near room temperature), the product velocity distributions are statistical as modeled by classical phase space theory (which disagrees with the metastable ion dissociation work but might be explained by the different experimental conditions).²⁷ However, at slightly higher kinetic energies, the product velocity distributions quickly become non-isotropic and show direct forward scattering of the CH_3Cl product relative to the Cl^- vector. That is definitely non-statistical behavior. At still higher kinetic energies, a new rebound mechanism is indicated by backward scattering.²⁵

We further applied product velocity distribution measurements to reaction (10) with $RH = CH_4$ and C_2H_6 .²³ These experiments showed definitively that the reactions are non-statistical. We observed non-isotropic scattering (relative to the center-of-mass of the system), proving a

direct reaction mechanism. The product velocities approach the spectator stripping limit at high collision energies.²³ This result corroborates our observation of apparent threshold energies well in excess of the calculated potential energy barriers. This is an interesting result fundamentally, but it means that we cannot model the product velocities with statistical phase space theory to extract barrier heights as we had hoped. In principle, the cross sections and product velocity distributions could be modeled by classical or quantum trajectory calculations; however, besides being computationally expensive that would require an accurate potential energy surface, whereas our aim is application to systems where the potential energy surface is not easily obtainable and the endoergicity is unknown. However, it may be useful to apply product velocity distribution measurements in the future in systems that appear to behave statistically, in particular for collision-induced dissociation systems.

3.5. Negative Ion Photoelectron Spectroscopy

The radical electron affinity is an essential component of the negative ion thermochemical cycle for determining neutral radical energetics. We primarily rely on electron affinity measurements obtained by a number of excellent groups doing negative ion photoelectron spectroscopy.³⁵⁻⁵⁰

We have also collaborated with Prof. W. Carl Lineberger at the University of Colorado, Boulder, on negative ion photoelectron spectra of systems of relevance to combustion kinetics. During a sabbatical visit by the PI in Boulder, we obtained spectra of the naphthide anion, $C_{10}H_7^-$.⁵¹ Because of a large number of active modes, this has a fairly broad and congested spectrum, although the origin transition is partially resolved. To confirm the origin assignment and to extract an accurate electron affinity, new Franck-Condon fitting procedures had to be developed. The PESCAL program⁵² was completely revised to allow Franck-Condon fits with treatment of Dushinsky rotation for all 45 modes of $C_{10}H_7^-$. The vibrational frequencies and normal mode vectors were obtained from density functional theory (B3LYP/aug-cc-pVDZ). Naphthide is likely the largest low-symmetry molecule for which a full Franck-Condon treatment with Dushinsky rotation and including all modes has been performed. A heuristic algorithm was developed to identify the important transitions for the Franck-Condon overlap calculation; otherwise the number of overlap integrals for combination band transitions is overwhelming for a large molecule. The electron affinity determined in this work, $EA(C_{10}H_7) = 1.403 \pm 0.015$ eV, was combined with literature values of the gas-phase acidity to obtain a new bond dissociation energy, $D(C_{10}H_7-H) = 472 \pm 14$ kJ/mol. The new PESCAL program⁵² has been provided to eight research groups internationally.

In 2003, we published a photoelectron spectrum of O_2^- .⁵³ The purpose of this work was to definitively establish the electron affinity of O_2 , which has been subject to erroneous revisions published recently by Chen and coworkers⁵⁴⁻⁵⁶ based on their Electron Capture Detector method. The proposition of Chen and coworkers that photoelectron spectroscopists had been observing solely an excited electronic state of the anion was refuted by means of a detailed spectroscopic analysis and by theoretical calculations in collaboration with Professor Jack Simons at the University of Utah and his coworkers.

3.6. Theoretical calculations

Theoretical calculations are applied throughout our work to complement the experiments. Both bimolecular reactions and collision-induced dissociation processes are modeled with statistical rate theory.^{22,23,25,57,58} The transition state parameters including geometries and frequencies are obtained using electronic structure calculations, typically density function theory (e.g., using the hybrid functional B3LYP). Calculated potential energy surfaces for our reaction

help inform our statistical rate theory analyses and understand reaction mechanisms and dynamics. The thermochemical results are compared with either composite models (Gaussian3 or CBS) or coupled-cluster theory (CCSD(T)). For gas-phase acidities, we have compared the performance various levels of theory on a series of evaluated benchmark species.¹² We found that obtaining accurate gas phase acidities of benchmark species within a few kJ/mol requires calculations at least at the CCSD(T)/aug-cc-pVTZ level, whereas the less expensive composite models have larger systematic and random errors. The CCSD(T) calculations with large basis sets are still impractical for asymmetric systems with more than 5–6 heavy atoms.

3.7. Kinetic Method

The so-called “kinetic method” is a popular technique in the mass spectrometry community for determining ion affinities (e.g., proton affinities or gas-phase acidities).⁵⁹⁻⁶² It involves measuring the branching ratio for the metastable dissociation or collision-induced dissociation of an ion-bound heterodimer, for example, $A-M^+-B_i$ into $AM^+ + B_i$ and $A + MB_i^+$, where the M^+ -affinity of A is the unknown and those of a series of compounds B_i are used for calibration. A correlation plot is based on the thermodynamic formulation of transition state theory, $\ln(I_A/I_{B_i}) = \Delta\Delta H/RT_{\text{eff}} - \Delta\Delta S/R$, where the I_A and I_{B_i} are the AM^+ and B_iM^+ ion abundances in the mass spectrum, $\Delta\Delta H$ is the enthalpy difference between the two channels (ion affinity difference, assumed to be the same as the transition state energy difference), and T_{eff} is called the “effective temperature” but is just a correlation parameter. The kinetic method, especially an extended method to measure the $\Delta\Delta S$ entropy term, has generated a continuing controversy among practitioners and critics,⁶²⁻⁷¹ in part because its claimed accuracy and precision have been overrated.

Our competitive threshold collision-induced dissociation technique is superficially similar to the kinetic method, but has the advantage of making the competitive dissociation measurements over a very wide range of energies (rather than one or a few energies in the kinetic method) and modeling the branching ratios with a full statistical rate theory analysis (namely, with RRKM theory and including all experimental energy broadening effects). Fitting the product branching ratio over a broad range of energies provides a good internal test of the model, which is absent in the kinetic method. Because we already had the theoretical tools for modeling statistical dissociation of ion-molecule complexes, we have examined the physical basis for the kinetic method in a series of papers addressed primarily to mass spectrometrists.^{57,58,72} These papers attempt to show why the “effective temperature” should not be treated as a thermodynamic temperature, and to provide realistic uncertainty estimates for kinetic method treatments. As part of the latest work,⁵⁸ we have also created a program for multiple regression fitting of kinetic method data with a proper statistical treatment.⁷³

4. Personnel

The following personnel were funded as participants in the research project:

Kent M. Ervin, Principal Investigator
Dr. Yang Shi, Postdoctoral Research Associate
Dr. Laurence A Angel, Postdoctoral Research Associate
Dr. F. Ahu Akin, Postdoctoral Research Associate
Nicholas A. Sassin, Chemical Physics Ph.D. candidate
Moses K. Dogbevia, Chemical Physics Ph.D. candidate

The following personnel participated, but without direct funding:

Brain Hoyt, Undergraduate Research Student

Sandra P. Garcia, Undergraduate Research Student

5. Financial

The contracted funds were fully expended as of the end date, June 30, 2004.

6. Renewal

This grant project ends as of June 30, 2004. In lieu of a continuation renewal proposal, a proposal for a new project extending the work is being submitted in August 2004.

7. References

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